ARMY RESEARCH LABORATORY

Synthesis and Characterization of Partial Biobased Furan Polyamides

by LaShonda T. Cureton and John J. La Scala

ARL-TR-6828 **February 2014**

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-TR-6828 **February 2014**

Synthesis and Characterization of Partial Biobased Furan Polyamides

LaShonda T. Cureton
Oak Ridge Institute

John J. La Scala
Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
February 2014	Final	July 2012

4. TITLE AND SUBTITLE
Synthesis and Characterization of Partial Biobased Furan Polyamides

5a. CONTRACT NUMBER
1120-1120-99

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
MMB104

6. AUTHOR(S)
LaShonda T. Cureton* and John J. La Scala

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: RDRL-WMM-C
Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-6828

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
*Oak Ridge Institute for Science and Education, 1299 Bethel Valley Rd., Oak Ridge, TN 37830

14. ABSTRACT
We have used two synthetic methods, "direct" polycondensation and interfacial polymerization, to prepare partially biobased furan polyamides from the biobased monomer, 2,5-furan dicarboxylic acid, a product of carbohydrates, and *p*-phenylenediamine. Polyamides synthesized from interfacial polymerization provided consistent molecular weight values averaging 24,000 g/mol. These materials show limited solubility in some organic solvents like acetone and chloroform; however, they are highly soluble in sulfuric acid and polar aprotic solvents anhydrous dimethylformamide, anhydrous 1-methyl-2-pyrrolidinone, and dimethyl sulfoxide. Thermal analysis measurements of the partially biobased polyamides have shown an average thermal stability of 400 °C, compared to that of manufactured petroleum-based Kevlar (T_d, 427°–482 °C), and T_g values have been observed to be greater than the degradation of the polymer materials.

15. SUBJECT TERMS
biobased polymers, Kevlar, furan, carbohydrates, titration

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			John. J. La Scala
Unclassified	Unclassified	Unclassified	UU	22	19b. TELEPHONE NUMBER (*Include area code*) 410-306-0687

Contents

List of Figures

List of Tables

Acknowledgments

This work was supported in part by an appointment to the Postgraduate Research Participation Program at the U.S. Army Research Laboratory (ARL) administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Defense and ARL. The authors would like to thank Joseph Dougherty, Robert Lambeth, Rose A. Pesce-Rodriguez, and Eugene Napadensky.

1. Introduction

Production of polymeric materials derived from plants and other renewable resources has become a major research initiative in the last decade. The major driving force behind this research focus is primarily due to the rising costs of petroleum manufacturing—oil extraction and refining—and transportation to the United States and other countries (*1*). Additionally, there have been increased environmental concerns due to recent oil spills and seepage into the waterways and potable water systems (*2*). These issues present the need for developing high-strength and high-performance polymeric materials from sources other than petroleum chemicals. Kevlar* is among the highest performing engineering polymeric materials, having good structural and thermal integrity, but it is produced from and processed in petroleum-derived chemicals. The desire to develop materials derived from renewable resources, like Kevlar and its properties, is of great interest; however, the literature detailing such materials is limited. Research by Gandini and coworkers (*3, 4*) is likely one of the most thorough investigations of polymers that structurally mimic the sp^2 hybridization of Kevlar. The polyamide contains the biobased monomer 2,5-furan dicarboxylic acid, a product of carbohydrates, and *p*-phenylenediamine to make an analog of Kevlar. The polyamide was shown to have a thermal stability of 445 °C and a T_g of 325 °C. Yet the literature is lacking in further characterization of this material.

We seek to further develop these biobased furan analogs to Kevlar with the goal of obtaining polymers with high T_g and optimal mechanical properties. Furan has been investigated in chemical syntheses for specialty chemicals and polymers (*5, 6*). It is an attractive compound because it is chemically obtainable through the catalytic decarbonylation of furfural, which is obtained through chemical modification of hemicelluloses (xylose) (*6*). Functional furan derivatives, such as 5-hydroxymethylfurfural (HMF), are prepared through dehydration of glucose (*7*–*9*). The major source of glucose is vegetable products like corn, which is an abundant renewable resource. The United States produced approximately 320 million tons of corn from 2010 to 2012 (*10*), so there should be no difficulty in obtaining furan and its derivatives for large- and small-scale resins and polymers. This research intends to develop a series of high molecular weight biobased Kevlar analogs from two methods: (1) "direct" polycondensation and (2) interfacial polymerization of the biobased monomer 2,5-furan dicarboxylic acid and *p*-phenylenediamine with a high range of thermal properties and the ability to have mechanical stability equivalent or better than commercial polyamides.

*Kevlar is a registered trademark of E.I. DuPont de Nemours & Co., Inc.

2. Experimental

2.1 General Methods and Materials

Anhydrous 1-methyl-2-pyrrolidinone (NMP), pyridine, *p*-phenylene diamine, concentrated hydrochloric acid (HCl), thoinyl chloride, anhydrous dimethylformamide (DMF), chloroform, and tetrabutylammonium bromide (TBAB) were all purchased from Sigma-Aldrich and used as received. Methanol, lithium chloride (LiCl), hexane, and dimethyl sulfoxide (DMSO) were received from Fisher Scientific. 2,5-furan dicarboxylic acid was purchased from AK Scientific, Inc., and used as received. Sodium hydroxide was purchased from Fluka and used as received.

2.2 "Direct" Polycondensation of Partial Biobased Furan Polyamides

The partial biobased furan polyamides were prepared according to the literature using "direct" polycondensation using a Yamazaki-Higashi phosphorylation reaction (*11–13*) (figure 1). Polyamides were prepared in a three-neck 100-mL round-bottom flask equipped with a mechanical stirrer and gas inlet. 2,5-furan dicarboxylic acid (2.00 g, 12.8 mmol), *p*-phenylene diamine (1.42 g, 13.1 mmol), LiCl (0.55 g, 12.9 mmol), NMP (10 mL), and pyridine (7 mL) as a azeotroping agent, were added to the flask. The mixture was stirred 25–30 min at 100 °C, and then the temperature was ramped to 110 °C. After 1 h, the temperature was ramped again to 140 °C and the catalyst, triphenyl phosphite (6.4 mL), was added to the mixture. The reaction rapidly changed from a medium brown color to a dark green. The reaction temperature was ramped twice more to achieve a final temperature of 185 °C, and the mixture was allowed to soak overnight at that temperature. The reaction contents were precipitated into aqueous HCl solution dropwise, forming dark green to brown solids. The material was filtered and washed with methanol (50 mL, three times). The product was dried in an oven at 80–90 °C overnight under reduced pressure.

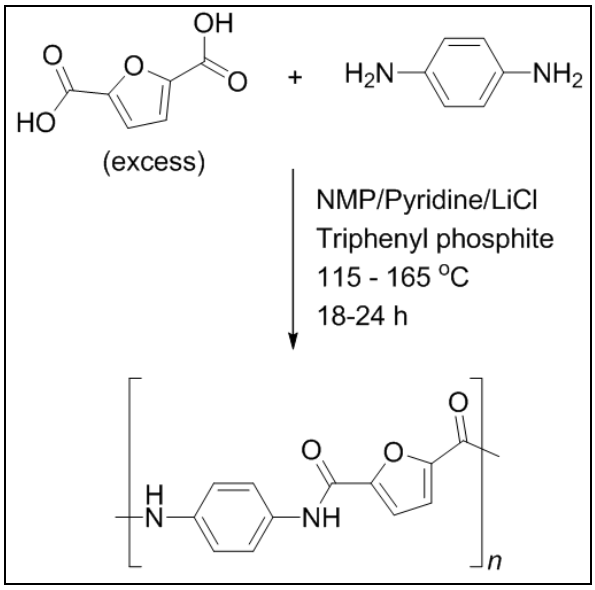

Figure 1. Synthetic routes for biobased furan polyamides using "direct" polycondensation.

2.3 Synthesis of 2,5-Furan Dicarboxylic Acid Chloride

The diacid chloride was synthesized from 2,5-furan dicarboxylic acid (*1*) (2.0 g) and thoinyl chloride (18 mL). The reagents were added to a 100-mL two-neck round-bottom flask equipped with a condenser and a trap filled with methanol. The solution was stirred at reflux (78–80 °C) for 3–5 h. After that time, anhydrous DMF (0.1 mL) was added to the solution as a catalyst and allowed to continue stirring for 2 h. The thionyl chloride was further distilled, and the product precipitated from solution and used without further purification. The white solid product was produced in a quantitative yield of greater than 95%. Characterization by ^{1}H NMR (DMSO-d_6 600 MHz) δ 7.52 ppm: (s, 2H, Ar-H).

2.4 Interfacial Polymerization of Partial Biobased Furan Polyamides

The general synthesis figure is described in figure 2. The partial biobased furan polyamides were prepared through interfacial polymerization described by Gandini and coworkers in the literature (*3, 4*). Biobased furan polyamides were prepared through interfacial polymerization in a three-neck 100-mL round-bottom flask equipped with a mechanical stirrer and N_2 gas inlet. Aromatic diamines (*p*-phenylenediamine) (2–5 g), 5-wt% TBAB catalyst (0.25–0.5 g), and 0.15- to 0.20-M NaOH solution (15–20 mL) were added to the flask and stirred at room temperature under nitrogen until all components were completely dissolved. The 2,5-furan dicarboxylic acid chloride (*2*) (4–6 g) was dissolved in chloroform (15–20 mL) and added in aliquots to the stirring diamine solution. Evolution of HCl gas occurred upon addition and continued until several minutes after all acid chloride solution was added. The reaction was allowed to stir for 2 h. The solid polymer was filtered and thoroughly washed with water (200 mL) and acetone (100 mL). The polymer was then dissolved in DMSO and stirred

overnight. The solution was filtered to remove any insoluble material and the solution was precipitated into water (500 mL). The biobased furan polyamide was filtered and dried under vacuum at 105–120 °C.

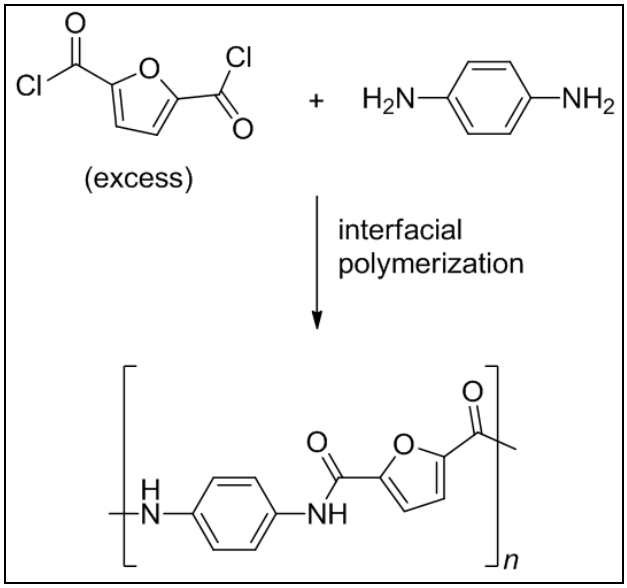

Figure 2. Interfacial polymerization for biobased furan polyamides.

3. Characterization Methods

3.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker 600-MHz spectrometer at 25 °C. Solutions containing 0.1%–0.5% monomer in deuterated methanol and 0.1%–0.5% polyamide in deuterated DMSO were used to measure the ^{1}H NMR spectra.

3.2 Size Exclusion Chromatography (SEC)

The SEC system used in this study was a Waters system composed of Waters 717 plus Autosampler held at 40 °C, Waters 510 Pump, and Waters 410 Refractive Index Detector held at 40 °C. Two columns (300 × 7.6 mm) held at 40 °C were used to separate molecular weights, Phenogel 5µ 10^4 Å and Phenogel 5µ 500Å. The solvent used was helium-purged DMF with LiCl salt at 0.06M, pumped at 1 mL/min. Relative molecular weights were determined by calibration with polystyrene narrow molecular weight standards. There was a mix of four standards in DMF with 0.06M LiCl: 51,000; 20,400; 5,050; and 580 amu. Standard 580 amu had to be rejected from calculations due to blockage by the solvent front. Because this molecular weight is far outside the desired molecular weights for the polyamides, there was little concern with rejecting this standard. This standard mix was injected (50 µL) every four unknown injections and compared. Results were satisfactory for the analysis (R^2= 0.998).

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were collected using a FTIR spectrometer (Thermo Nicolet Nexus 870 ESP) for 64 scans at 2-cm^{-1} resolution. FTIR data was processed using Thermo Nicolet's OMNIC spectroscopy software.

3.4 Thermal Analysis

Thermal stability was measured using a TA Instruments Hi-Res thermogravimetric analysis (TGA) 2950 at temperatures from 100 °C to 600 °C under nitrogen at a heating rate of 10 °C/min. Glass transition temperatures were measured on a TA Instruments differential scanning calorimetry (DSC) Q500 using a custom method with a heat/cool/heat cycle. A heating temperature ramp at 20 ºC/min from 25 ºC to 350 ºC and a cooling rate of 10 ºC/min was applied for the polyamides. These conditions were chosen to resolve all transitions that were not well defined at slower heating rates, and to avoid decomposition of the polymer at temperatures above 350 ºC. The glass transition temperature T_g was taken as the point of inflection automatically calculated using TA Instruments thermal analysis software by defining the limits of the glass transition region.

4. Results and Discussion

4.1 Synthesis Partial Biobased Furan Polyamides by "Direct" Polycondensation

Partial biobased furan polyamides were prepared by "direct" polycondensation using a Yamazaki-Higashi phosphorylation reaction (*11–13*). The reaction between *p*-phenylenediamine and 2,5-furan dicarboxylic acid was conducted in NMP with pyridine, as an azeotroping agent, LiCl, a salt, and a triphenyl phosphite condensation agent. The method used the diacid instead of a moisture-sensitive acid chloride because it is less susceptible to hydrolysis in the condensation reaction. The Yamazaki-Higashi phosphorylation reaction works by use of the triphenyl phospihte condensation agent, which is described to form a complex with pyridine in the presence of water. This method, which is well understood and has been described in Gandini et al.'s publication of furanic polyamides (*3*, *4*), is used by researchers preparing novel polyamides with variations of carboxyphenoxy benzenes (*14*), polyamides incorporating thiophene units (*15*), and –poly(amide-imide) copolymer systems (*16, 17*). However, there are disadvantages using this method, including side reactions from the phosphorylation that could create a large stoichiometric imbalance leading to decreased molecular weights of the polymer.

4.2 Synthesis of Partial Biobased Furan Polyamides by Interfacial Polymerization

The partial biobased furan polyamides were also synthesized via interfacial polymerization. Interfacial polymerization has been shown to be very efficient in producing polyamides of varying monomer groups in a short period of time without employing extreme synthetic conditions (*18–24*). The reaction used a 15%–20% NaOH aqueous solution to dissolve the diamine and 5-wt% TBAB as a phase-transfer catalyst to keep the diacid chloride monomer predominately in the organic layer to reduce the amount of hydrolysis that would occur in the aqueous layer. The organic solvent of choice was chloroform for the 2,5-furan dicarboxylic acid chloride because it provided greater solubility than chlorobenzene and had a reduced likelihood of hydrolyzing the acid chloride back to the acid precursor relative to dichloromethane. This method was chosen because it afforded high-molecular-weight polyamides of a different type synthesized by our group. Gandini et al. had published a similar interfacial method in the literature in which partial biobased furan polyamides were prepared having an inherent viscosity of 0.04–0.15 dl/g, although no molecular weight analysis was performed (*3, 4*).

4.3 Analytical Characterization of the Partial Biobased Furan Polyamides

The resulting partial biobased furan polyamides were characterized via NMR and FTIR to determine molecular structure. Indicated in figures 3 and 4 are the spectra itemizing the peaks that represent key functional groups of the polymer. The ^{1}H NMR of the polymer was analyzed from DMSO solvent, and the analysis produced a spectrum that showed peaks that were in good agreement with the chemical structure of polymer. The proton bonded to the nitrogen is featured at 10.42 ppm (s, 2H); the protons in the furan rings are featured at 7.42 ppm (s, 2.04H); and the protons in the aromatic unit are represented by the peaks at 7.80 ppm (d, 3.84H). Similarly, the ^{13}C NMR of the polymer was analyzed from DMSO solvent also. The peaks of the carbons in the polymers are shown at 130, 129.83, 116.42, 121.60, and 129.83 ppm, all from the aromatic ring; at 155.90 ppm, representing the carbonyl group; and at 148.75, 115.67, and 134.73 ppm of the furan ring. The spectra indicate no presence of side reaction occurring in the reaction and correspond to the spectra captured by Gandini and coworkers (*3*). The FTIR spectrum in figure 3 shows the key functional groups. The proton bond to the nitrogen is featured at 3354 cm^{-1}; amide groups are shown in the 1600 to 1300-cm^{-1} region; and the peaks representing the furan are shown in three locations: at 3135 cm^{-1}; 1547 cm^{-1}, indicating the C = C group in the furan and the furan units at 1021–760 cm^{-1}. The amide peaks are also featured in three locations: 1670, 1517, and 1316 cm^{-1}. The interpretation of these spectra corresponds to previous literature findings and shows successful formation of furan polyamides (*25*).

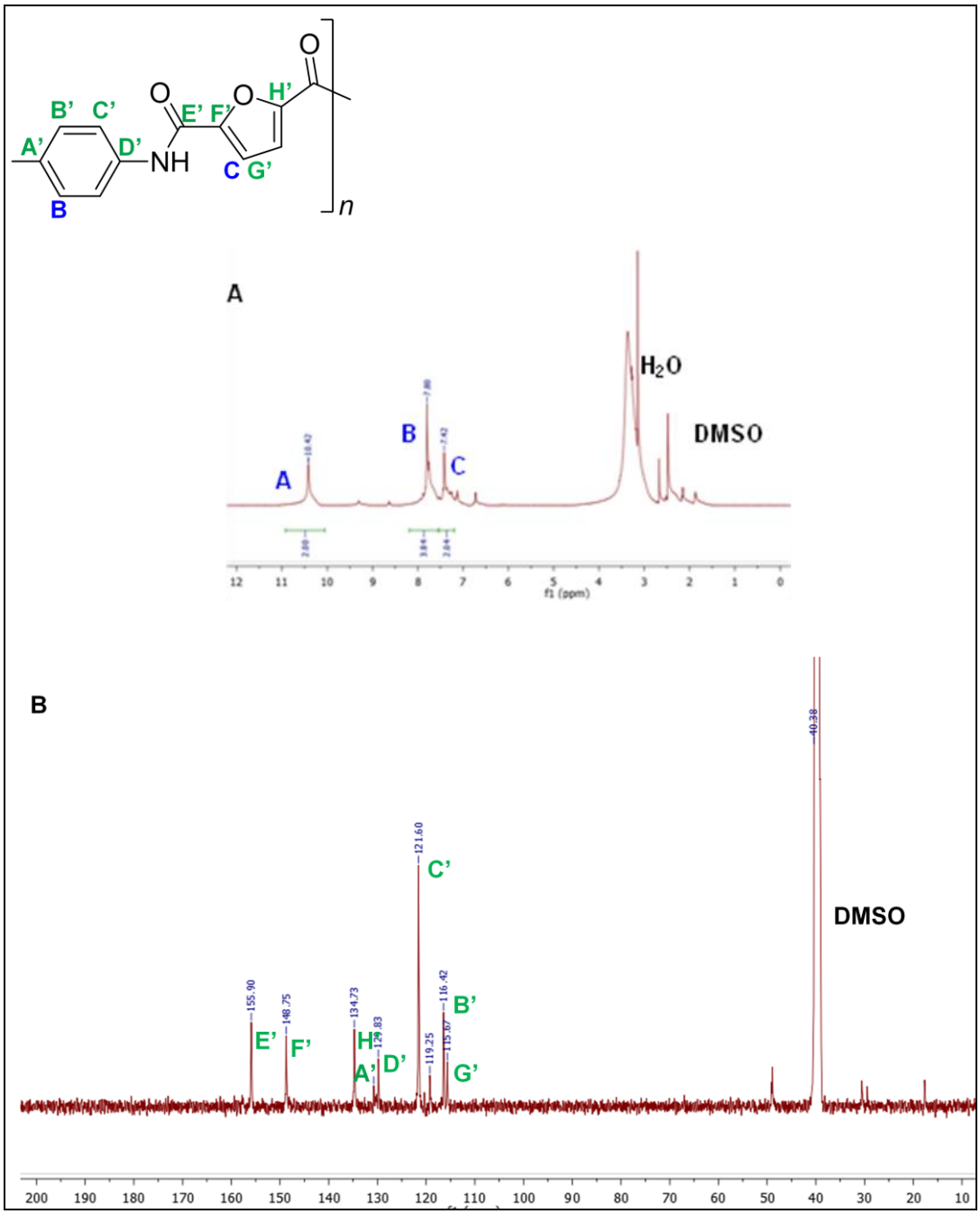

Figure 3. (A) ^{1}H and (B) ^{13}C NMR characterization of the partial biobased furan polyamides.

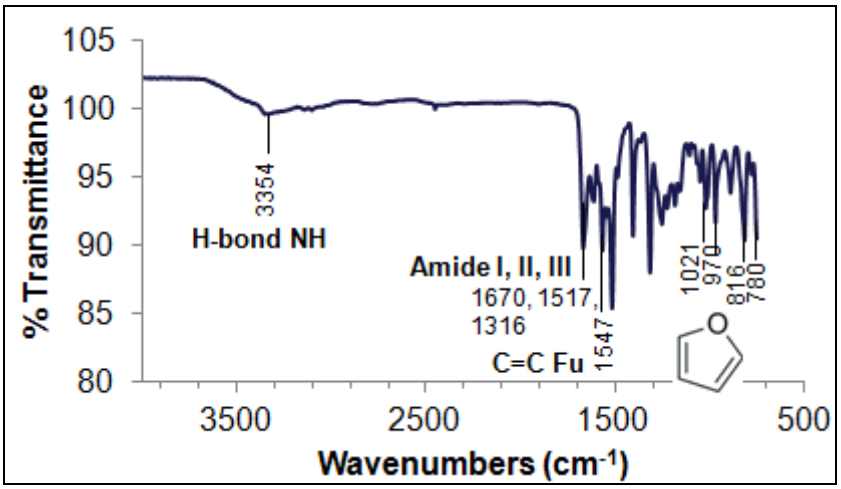

Figure 4. FTIR characterization of the partial biobased furan polyamides.

4.4 Solubility of the Partial Biobased Furan Polyamides

Kevlar is processed from fuming sulfuric acid because it is in soluble in water or organic solvents. The biobased Kevlar analogs demonstrated good chemical resistance in most organic solvents including acetone, methanol, and tetrahydrofuran (THF) (table 1). Like Kevlar, partial biobased furan polyamides were also soluble in concentrated sulfuric acid; however, they are soluble in solvents that Kevlar is not. They are completely soluble in polar aprotic solvents like DMSO, DMF, and NMP. They were also soluble in hexafluoroisopropanol. The enhanced solubility of the partial biobased furan polyamides provides enhanced processing capabilities through use of moderate boiling point solvents and without high-temperatures conditions and helps reduce the environmental impact from the use of hazardous solvents.

Table 1. Solubility of biobased Kevlar analogs.

Solvent	Partial Biobased Furan Polyamides	Kevlar
Acetone	—	—
Acetic acid	—	—
Chlorobenzene	—	—
Concentrated sulfuric acid	+	+
Dimethylformamide (DMF)	—	—
Dimethylsulfoxide (DMSO)	+	—
Hexafluoroisopropanol	+	—
Methanol	—	—
N-methyl-2-pyrrolidone (NMP)	+	—
Tetrahydrofuran (THF)	—	—

Note: + = soluble at room temperature; — = insoluable at room temperature.

4.5 Molecular Weight and Thermal Analysis of the Partial Biobased Furan Polyamides

The molecular weight of these partial biobased furan polyamides were measured by SEC and calculated based on a polystyrene standard calibration reference. The molecular weights of these polymers in table 2 were different based on the synthetic procedure used to prepare the polymers. Polymers prepared from "direct" polycondensation produced molecular weight values that were inconsistent and ranged from 6900 to 47,800 g/mol. The synthetic method used to prepare these polymers likely generated side reactions during the phosphorylation reaction that could have created a stoichiometric imbalance resulting in lower molecular weights. Polymers prepared from interfacial polymerization consistently resulted in an average molecular weights of 24,000 g/mol with polydisperity indexes (PDIs) corresponding with polymers synthesized via condensation reactions (PDI = 2.0). The differences in these measurements suggest that the interfacial polymerization is a better method for preparing these polymers since consistent molecular weights and appropriate distributions can be achieved.

The biobased furan polyamides also displayed good thermal properties as determined by TGA and DSC. Similar to the SEC data, the synthetic procedure also played a role in the extent of the thermal properties. The "direct" polycondensation method resulted in polymers with varying T_d and T_g that clearly showed a molecular weight dependence, with a critical molecular weight in the range of 15,000–30,000 g/mol. Above that critical molecular weight, T_g was greater than T_d and T_d was approximately 300 °C. Interfacial polymerization produced polymers with nearly identical degradation temperatures of approximately 370 °C and $T_g > T_d$. Again, based on these results, it seems likely that interfacial polymerization produces more consistent and higher performing furan-based polyamides with fewer side reactions. These polyamides did not display a melting temperature, indicating they are fully amorphous materials.

Table 2. Molecular weight and thermal properties of biobased furan polyamides.

M_n (g/mol)	M_w (g/mol)	PDI	T_g (°C)	$T_{d\text{-}5\ wt\text{-}\%}$ (°C)	$T_{d\text{-}max}$ (°C)	M_n (g/mol)
Solution Polymerization						
6900	11,300	1.65	292	266	416	6900
7800	13,300	1.70	296	278	437	7800
8800	33,600	3.81	$T_g > T_d$	310	442	8800
16,300	39,400	2.42	$T_g > T_d$	303	446	16,300
47,800	95,400	2.00	$T_g > T_d$	299	436	47,800
Interfacial Polymerization						
22,300	40,000	1.79	187	368	464	22,300
24,000	43,200	1.80	198	373	461	24,000
24,900	42,700	1.72	185	368	468	24,900

5. Conclusions

Partial biobased furan polyamides were synthesized using two synthetic methods, “direct” polycondensation and interfacial polymerization. The polymers synthesized in this research study were characterized for their chemical stability in various solvents and demonstrated improved solubility characteristics relative to analogous petroleum-based polymers such as Kevlar. These solubility features should allow the biobased materials enhanced processability options and remove the use of strongly hazardous solvents and high temperatures. These materials also showed thermal stability at high temperatures to nearly 400 °C. These partial biobased furan polyamides were fully amorphous polymers with a high T_g.

6. References

1. *U.S. Crude Oil, Natural Gas, and NG Liquids Proved Reserves.* U.S. Energy Information Administration, Analysis & Projections, U.S. Department of Energy, 27 February 2012. http://www.eia.gov/analysis/ (accessed 9 July 2012).
2. *Oil Spills*. U.S. Environmentatal Protection Agency, 13 December 2011. http://www .epa.gov/oilspill/ (accessed 24 January 2013).
3. Mitiakoudis, A.; Gandini, A. Synthesis and Characterization of Furanic Polyamides. *Macromolecules* **1991,** *24,* 830.
4. Mitiakoudis, A.; Gandini, A.; Cheradame, H. Polyamides Containing Furanic Moieties. *Polym. Commun.* **1985,** *26,* 246.
5. Saladino, R.; Pagliaccia, T.; Argyropoulos, D. S.; Crestini, C. Production of Chemicals From Cellulose and Biomass-Derived Compounds: Advances in the Oxidative Functionalization of Levulinic Acid. *ACS Symp. Ser.* **2007,** *954,* 262.
6. Lichtenthaler, F. W. Industrial Chemicals From Carbohydrate Feedstocks: Current Status and Challenges Ahead. In *Production of Fuels, Specialty Chemicals and Biobased Products From Agro-Industrial Wastes and Surplus;* Fava, F., Carepa, P., Eds.; INCA: Venezia, Italy, 2008; pp 230–253.
7. Lucia, L. A.; Argyropoulos, D. S.; Adamopoulos, L.; Gaspar, A. R. Materials and Energy from Biomass: A Review. In *Materials, Chemicals, and Energy from Forest Biomass;* Argyropoulos, D. S., Ed.; American Chemical Society: Washington, DC, 2007; p 2.
8. Martin, D.; Lichtenthaler, F. W. Versatile Building Blocks From Disaccharides: Glycosylated 5-hydroxymethylfurfurals. *Tetrahedron: Asymmetry* **2006,** *17,* 756.
9. Gandini, A. Furans as Offspring of Sugars and Polysaccharides and Progenitors of a Family of Remarkable Polymers: A Review of Recent Progress. *Polym. Chem.* **2010,** *1,* 245.
10. *National Statistics for Corn*. National Agriculture Statistics Service, U.S. Department of Agriculture, 2012. http://www.nass.usda.gov/Statistics_by_Subject/ (accessed 24 January 2013).
11. Higashi, F.; Taguchi, Y. Aromatic Polyamides by Phosphorylation Reaction With Triphenylphosphite and LiCl in the Presence of Polymer Matrix. *J. Polym. Sci., Polym. Chem. Ed.* **1980,** *18,* 2875.
12. Higashi, F.; Taguchi, Y. Effects of the Rates of Initiation and Propagation on a Direct Polycondensation Reaction With Triphenyl Phosphite and Pyridine. *J. Polym. Sci., Polym. Chem. Ed.* **1981,** *19,* 3345.

13. Higashi, F.; Taguchi, Y.; Kokubo, N.; Ohta, H. Effect of Initiation Conditions on the Direct Polycondensation Reaction Using Triphenyl Phosphite and Pyridine. *J. Polym. Sci., Polym. Chem. Ed.* **1981,** *19,* 2745.

14. Zhao, J.; Xu, H.; Fang, J.; Yin, J. Synthesis and Characterization of Novel Aromatic Polyamides via Yamazaki-Higashi Phosphorylation Method. *J. Appl. Polym. Sci.* **2012,** *126,* 244.

15. Ubale, V. P.; Sagar, A. D.; Maldar, N. N.; Birajdar, M. V. Synthesis and Characterization of Aromatic-Aliphatic Polyamides. *J. Appl. Polym. Sci.* **2001,** *79,* 566.

16. Avella, N.; Maglio, G.; Palumbo, R. Poly(amideimide)s Based on Diamines Containing Bisaryloxy Groups: Structure-Properties Relationships. *J. Polym. Sci., Part A: Polym. Chem.* **1996,** *34,* 1219.

17. Simionescu, M.; Marcu, M.; Cazacu, M. New Poly(amide-imide) SiloxaneC by Polycondensation. *Eur. Polym. J.* **2003,** *39,* 777.

18. Beaman, R. G.; Morgan, P. W.; Koller, C. R.; Wittbecker, E. L.; Magat, E. E. Interfacial Polycondensation. III. Polyamides. *J. Polym. Sci.* **1959,** *40,* 329.

19. Wittbecker, E. L.; Morgan, P. W. Interfacial Polycondensation, I. *J. Polym. Sci.* **1959,** *40,* 289.

20. Kwolek, S. L.; Morgan, P. W. Preparation of Polyamides, Polyurethanes, Polysulfonamides, and Polyesters by Low Temperature Solution Polycondensation. *J. Polym. Sci.* **1964,** *Pt. A 2,* 2693.

21. Morgan, P. W.; Kwolek, S. L. Interfacial Polycondensation, 2. Fundamentals of Polymer Formation at Liquid Interfaces. *J. Polym. Sci.* **1959,** *40,* 299.

22. Morgan, P. W.; Kwolek, S. L. Interfacial Polycondensation,12. Variables Affecting Stirred Polycondensation Reactions. *J. Polym. Sci.* **1962,** *62,* 33.

23. Morgan, P. W.; Kwolek, S. L. Interfacial Polycondensation, 2. Fundamentals of Polymer Formation at Liquid Interfaces. *J. Polym. Sci., Part A: Polym. Chem*. **1996,** *34,* 531.

24. Wittbecker, E. L.; Morgan, P. W. Interfacial Polycondensation, 1. *J. Polym. Sci., Part A: Polym. Chem.* **1996,** *34,* 521.

25. Gharbi, S.; Afli, A.; El, G. R.; Gandini, A. Polyamides Incorporating Furan Moieties, 4. Synthesis, Characterisation, and Properties of a Homologous Series. *Polym. Int.* **2001,** *50,* 509.

NO. OF COPIES	ORGANIZATION
1 (PDF)	DEFENSE TECHNICAL INFORMATION CTR DTIC OCA
1 (PDF)	DIRECTOR US ARMY RESEARCH LAB IMAL HRA
1 (PDF)	DIRECTOR US ARMY RESEARCH LAB RDRL CIO LL
1 (PDF)	GOVT PRINTG OFC A MALHOTRA
11 (PDF)	RDRL WMM R DOWDING J ZABINSKI RDRL WMM A J SANDS RDRL WMM C J LA SCALA J SADLER RDRL WMM G J ANDZELM IN-CHUL YEH J DOUGHERTY E NAPADENSKY A RAWLETT B C RINDERSPACHER

INTENTIONALLY LEFT BLANK.